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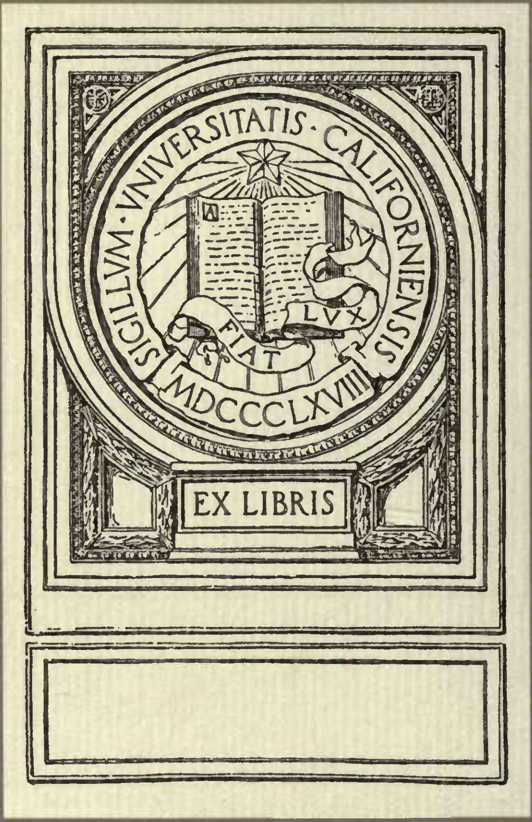
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EQUILIBRIA IN REACTIONS OF METHYL ALCOHOL WITH HYDROCHLORIC ACID AND WITH HYDROBROMIC ACID

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EQUILIBRIA IN REACTIONS OF METHYL ALCOHOL WITH HYDROCHLORIC ACID AND WITH HYDROBROMIC ACID.

UNIV. OF CALIFORNIA

This work is the beginning of a study of the reversible reactions of some of the simpler organic compounds, with a view to obtaining their free energies. In organic chemistry in particular, reactions in general are slow, and it is of great practical as well as theoretical importance, in the case of attempting to make a reaction take place, to know whether it fails because the velocity of the reaction is insufficient, or whether the reaction has no tendency to go in the desired direction, but tends on the contrary to go in the opposite direction.[1]

The free energies of only a few organic substances have as yet been measured, notably methane,[2] carbonyl chloride,[2] urea and ammonium cyanate,[3] and formic acid.[4]

The equilibria here measured form part of the experimental work necessary to determine the free energy of the important reactions of the alcohols. The reaction of hydrochloric acid and of hydrobromic acid with methyl alcohol is very slow, and from four to six days heating at 110°C was necessary to reach

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[1] An interesting case in point was the attempt of chemists during the war to find a catalyst to cause "phosgene" (carbonyl chloride) to polymerize to "diphosgene" (trichlormethylchlorformate), until it was shown that "diphosgene," with a suitable catalyst decomposed to phosgene, when, of course, the search was abandoned.

[2] Lewis and Randall, J. Am. Chem. Soc., 37, 458 (1915).

[3] Lewis and Burrows, Ibid., 34, 1515 (1912).

[4] Branch, Ibid., 37, 2316 (1915).

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equilibrium.[1)]

Experimental Procedure. Equilibrium measurements on the reactions $CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O$ and $CH_3OH + HBr \rightleftharpoons CH_3Br + H_2O$ were made at 110°C and at 140°C. The temperatures were measured by mercury thermometers which had been compared at the temperatures used, with a calibrated thermocouple. The measurements at 110°C were made in a small, electrically heated thermostat, with a mercury regulator. Mineral oils, and later "crisco" were tried as thermostat liquids, but both were abandoned on account of the excessive charring and gumming, especially on long continued use. Finally a mixture of calcium chloride and zinc chloride with water, nearly saturated at the working temperature, was tried and found very satisfactory, the only inconvenience being the necessity of replacing, every few days, the water lost by evaporation. The 140° thermostat was an air bath.

The temperature in the mixed chlorides varied only about a tenth of a degree from the mean, but the air bath varied about half a degree from the mean temperature. In both cases the make and break of the relay took place about once in two minutes, and the average temperature, taken over a short time, was constant for weeks. The large fluctuations in the case of the air bath is probably due to the lag in the mercury regulator, on account of the low heat conductivity of air, but since the reaction tubes

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[1)] The halogen acids react very slowly with alcohols in comparison with the oxy-acids, which react readily, forming esters. This is not due, however, to greater stability of the product formed, for the oxy-acid esters also hydrolyze more readily than the halogen esters. This marked difference in behavior is explained by assuming that the fast reaction of the alcohol is that in which it reacts as an acid, and the hydrogen of the alcohol combines with the hydroxyl group of the oxy-acid, while such a reaction with a halogen acid is impossible.

were subject to a like lag, the temperature in the tubes was probably far more nearly constant than that of the air. Furthermore, because of the failure of a slow reaction to respond to rapid changes of temperature, rapid fluctuations about a mean temperature are not of appreciable significance.

Mixtures were made up of the substances involved in the reaction, sealed in glass tubes, and heated until equilibrium was attained. Solutions of known composition were made by mixing weighed quantities of methyl alcohol, water, and hydrochloric (or hydrobromic) acid solution to obtain any desired mixture. Methyl chloride (or bromide) was not added to the mixtures because of the difficulty of controlling and measuring its concentration, owing to its volatility.

On account of the difficulty of analyzing for small amounts of methyl chloride or bromide, the concentration in the equilibrium mixture was determined by difference, from the initial and final concentrations of acid. This assumes that the only reaction, or at least the chief reaction, is :

$$CH_3OH + HCl = CH_3Cl + H_2O$$

(or the corresponding one with hydrobromic acid), and that a molecule of methyl chloride is formed for each molecule of hydrochloric acid used up. For this reason the effect of ordinary glass in neutralizing acid had to be avoided, and "Pyrex" glass was used throughout, because it was found that the solution products of "Pyrex" did not appreciably affect the acid concentration.

The concentrations of the methyl alcohol and the water were practically constant because of the small number of mols of each entering into the reaction, relative to the amounts present.

To simplify the interpretation of the results, the ratio of the methyl alcohol to the water was kept constant throughout the work. Since the fugacity of a gas is very nearly equal to its pressure, or, in other words, since gases, and even saturated vapors, at low pressures very closely obey the Mass Law, by measuring the partial vapor pressures of alcohol and of water over this mixture we can calculate the equilibrium for any other mixture provided the vapor pressures over the new mixture are known.

The acid concentration was sometimes measured by titration in cold solution with tenth-normal sodium hydroxide, and sometimes by measuring the electrical conductivity of the solution.

It was determined by preliminary experiments that, with a given ratio of methyl alcohol to water, the specific conductivity of the solution containing hydrochloric acid was quite closely proportional to the concentration of hydrochloric acid, in the dilute solutions used. Since the initial concentrations of the solutions were known, the final concentration of hydrochloric acid could thus easily be obtained by measuring the initial and final conductivities of the solution. This method was particularly convenient in that the hydrochloric acid concentration could be determined at any stage of the reaction without destroying the reaction mixture, and thus it could be ascertained that each individual mixture was approaching equilibrium, by the approach of its conductivity to constancy.

As before mentioned, the cells were made of "Pyrex" glass on account of the fact that it neutralizes the acid much less than does soft glass, and it was found possible to seal platinum

electrodes into the tubes, in spite of the considerable difference in the coefficients of expansion of the platinum and the glass. However, in some of the cells it was found that there was sometimes a very slight leak, estimated in one experiment to be about 0.04 cc. in about four days heating at 110°C, and about two atmospheres difference in pressure.

While it is believed that most of the carefully made cells did not leak, to avoid the necessity of giving a rigorous test to each cell, some of the reaction mixture was put in each of the lead "arms" of the cell, and sealed, so that the pressure on each side of the platinum seal was approximately equal.

The conductivities were not taken in the thermostats in which the reaction was taking place, because the temperature control was not good enough for accurate conductivity measurements, but when the conductivity was to be taken the cell was taken out of the thermostat and cooled quickly to prevent further reaction. Then the sealed leads were broken open, mercury contacts made with the electrodes, and the conductivity measured at 25°C, with the standard conductivity bridge. The conductivity measurements themselves could be made with far greater accuracy than was needed. When the measurement was completed, the leads were resealed and the cell returned to the thermostat.

In the cases where the reaction mixtures were titrated for the remaining hydrochloric or hydrobromic acid, it was found necessary to cool the tubes in a freezing mixture before opening them, to prevent loss by spattering, because at room temperature the total vapor pressure of the mixture is more than an atmosphere. The hydrolysis of the methyl chloride or bromide in the solution during titration is too slow at room temperature to cause appreciable error.

TABLE I.

Measurements on Reaction of Methyl Alcohol with Hydrochloric Acid.

Temperature 110°C, 0.914 mols alcohol/mol H_2O.

Expt. No.	Initial conc. HCl mols/1000 gm. solution.	Final conc. HCl mols/1000 gm. sol.	$\frac{MeCl}{(HCl)^2}$
1	0.0318	0.0283	4.49
2	0.0424	0.0366	4.32
3	0.0669	0.0545	4.18
4	0.0687	0.0557	4.19
5	0.1039	0.0789	4.02
	Mean of Constant		4.24

Temperature 140°C.

Expt. No.	Initial conc. HCl mols/1000 gm. solution	Final conc. HCl mols/1000 gm. solution	$\frac{MeCl}{(HCl)^2}$
1	0.0756	0.0383	25.4
2	0.1000	0.0457	26.0
3	0.1442	0.0581	25.5
	Mean of Constant		25.6

TABLE II.

Measurements on Reaction of Methyl Alcohol with Hydrobromic Acid.

Temperature 110°C. 0.914 mols methyl alcohol/mol H_2O.

Expt. No.	Initial conc. HBr mols/1000 gm. solution	Final conc. HBr mols/1000 gm. solution	$\frac{MeBr}{(HBr)^2}$
1	0.0372	0.0363	0.687
2	0.0909	0.0862	0.633
3	0.1834	0.1652	0.667
	Mean of Constant		0.662

Temperature 140°C

Expt. No.	Initial conc. HBr mols/1000 gm. solution	Final conc. HBr mols/1000 gm. solution	$\frac{MeBr}{(HBr)^2}$
1	0.0372	0.0339	2.87
2	0.0909	0.0862	2.66
3	0.1834	0.1366	2.51
	Mean of Constant		2.68

nothing missing

Discussion of Results. In Table I are given the results of equilibrium measurements made with the hydrochloric acid solutions. Concentrations are in mols per thousand grams of solution. The experiments were done in duplicate, and, in general, each number in the table represents the mean of duplicate determinations. As before stated, the methyl chloride concentration has been taken as equal to the difference between the initial and final concentrations of the hydrochloric acid, except for a small correction for acid neutralized by the glass.

It is notable that the quantity C_{MeCl}/C^2_{HCl} is practically constant. There appears to be a slight trend in the constant, especially in the values on hydrochloric acid at 110°C, the larger values appearing in the more dilute solutions. This might be explained by assuming that in the more concentrated solutions true equilibrium was not quite attained because the extent of the reaction necessary to attain equilibrium is greater both relatively and absolutely, in the more concentrated solutions. However, the reactions were followed by the conductivity method and the reaction adjudged complete only when there was no further change of acid concentration, as measured by the conductivity. The noticeable trend occurs especially in the very dilute solutions, where the difficulty of accurate analysis and the uncertainty in the correction for acid neutralized by the glass are both accentuated, and it is not deemed desirable to assume that the trend is a real onewithout further experiments.

At the concentrations used the vapor pressure(and hence the fugacity) of the methyl chloride is almost certainly proportional to the concentration of methyl chloride, and hence the vapor pressure of the hydrochloric acid from the solutions used is

approximately proportional to the square of its concentration, just as is the case in dilute water solutions of hydrochloric acid. This is not surprising, considering the fact that the mol fraction of water in the solution is greater than one-half, and methyl alcohol as a solvent is quite similar to water.

The above discussion applies equally well to the results on the reaction of methyl alcohol with hydrobromic acid, which appear in Table II.

The equilibrium constant is much larger at the higher temperature, indicating a large absorption of heat, as the reaction goes from left to right. From the results at the two temperatures, we can calculate the heat of the reaction by the van't Hoff Equation, $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$ ¹⁾ where ΔH is the increase in heat content of the system, or the negative of the "heat of reaction" at constant pressure. Thus we calculate for

$$CH_3OH + HCl = CH_3Cl + H_2O; \quad \Delta H = + 17600 \text{ cal.}$$

and for

$$CH_3OH + HBr = CH_3Br + H_2O; \quad \Delta H = + 13000 \text{ cal.}$$

In the above reactions all the substances are in solution. ΔH for the first reaction was calculated from the thermochemical data of Thomson and Berthelot, and found to be 17000 calories, a much closer agreement than could be expected. For the second reaction sufficient data were not found to calculate this heat from thermochemical measurements.

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1) This equation is strictly applicable only under the conditions that the pressure is constant. In the experimental work the pressure was equal to the total vapor pressure and was of course not constant. But the difference, even in the extreme case in which the volume was kept constant would be negligible, as the volume change in this reaction, as in most reactions not involving gases, is very small.

It is proposed in the near future to extend this work and calculate the free energy of these and of other reactions.

SUMMARY.

Equilibrium measurements have been made on the reactions

$$CH_3OH + HCl = CH_3Cl + H_2O$$

and

$$CH_3OH + HBr = CH_3Br + H_2O$$

with a view to obtaining the free energies of these reactions.

The concentration of methyl halide divided by the square of the concentration of halogen acid is found to be constant, indicating that the vapor pressure of halogen acid from the solution is proportional to the square of its concentration.

From measurements at two temperatures the change in heat content has been determined for the two reactions; for

$$CH_3OH + HCl = CH_3Cl + H_2O; \quad \Delta H = +17600 \text{ cal.};$$

for

$$CH_3OH + HBr = CH_3Br + H_2O; \quad \Delta H = +13000 \text{ cal.}$$

I wish in conclusion to express my indebtedness to Dr. G. N. Lewis and Dr. G. E. K. Branch, under whose direction the work was carried out, and to Dr. W. C. Bray, for valuable help and criticism.

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